New Chiral Cyclopentadienylrhenium Lewis Acids Featuring Fluorinated Triarylphosphanes and Enhanced Acceptor Abilities − An Unusual Carbon−Fluorine Bond Activation in a Metal Coordination Sphere

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Dedicated to Professor Dr. H.-J. Bestmann on the occasion of his 75th birthday

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The acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(NCCH_3)(CO)]^+ BF_4^-$ (**1**) and $P(4\text{-}C_6H_4CF_3)_3$ slowly react (2 d, room temperature) to give the substitution product $[(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(CO)]^+BF_4^-$ (**3**, 85%). The reaction of **1** and less nucleophilic $P(C_6F_5)_3$ must be conducted in a melt at 140 °C, but $[(\eta^5\text{-}C_5H_5)Re(NO)\{P(C_6F_5)_3\}(CO)]^+BF_4^-$ (**11**) is isolated in 90% yield. Reduction of **3** by $NaBH_4$ gives the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(CH_3)$, which is treated with TfOH and $H_3CN{=}C(H)C_6H_5$ to give the imine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{N(CH_3){=}C(H)C_6H_5\}]^+TfO^-$ (**9**). Complex **9** was, like the non-fluorinated analog, unreactive towards allyltin nucleophiles. Complex **11** should lead to a more reactive imine complex, but $NaBH_4$ gave a methyl complex that was difficult to purify. However, $NaOCH_3$ or $NaSCH_3$/methanol gave easily purified $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6F_4OCH_3)_3\}(CO_2CH_3)$ (85%) or $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6F_4SCH_3)_3\}(CO_2CH_3)$ (51%), in which all *para*-fluorine atoms have undergone nucleophilic displacements, and the carbonyl ligands methoxide additions. This suggests that catalytic chemistry of the chiral Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)\{P(C_6F_5)_3\}]^+$ (**I**-F_{15}) will be complicated by nucleophilic degradation. Nonetheless, density functional calculations show that **I**-F_{15} is a much stronger σ acceptor and weaker π donor than less fluorinated analogs.

Introduction

Numerous modern catalytic methods for enantioselective organic synthesis make use of chiral transition metal Lewis acids.[1] The optimization of their steric and/or electronic properties is essential for many processes. For example, the fine tuning of donor/acceptor characteristics was critical to the development of chiral cyclopentadienyliron and -ruthenium catalysts for highly enantioselective Diels−Alder cycloadditions.[2] In the same vein, there are a variety of chiral titanium(IV) catalysts that activate aldehydes towards enantioselective additions of allylstannanes.[1] However, more electrophilic, fluorinated titanium(IV) catalysts are required to promote analogous reactions of less nucleophilic but cheaper and more readily available allylsilanes.[3]

We have undertaken extensive studies of adducts of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) and unsaturated organic ligands such as aldehydes,[4] ketones,[5] alkenes,[6] and imines.[7] These are readily available in enantiomerically pure form, and stoichiometric additions of strong carbon nucleophiles often proceed with high diastereoselectivities.[4−7] However, weaker nucleophiles such as allylstannanes do not give rapid additions. In fact, rate experiments show that **I**, unlike many other transition metal Lewis acids, does not strongly activate unsaturated ligands towards nucleophiles. This has hampered the development of transformations that would be catalytic in rhenium.

The lack of activation can be ascribed to electronic properties of **I**. Most transition metal Lewis acids are best regarded as amphoteres. Except for d^0 systems, they have occupied d orbitals that are usually capable of backbonding to the acceptor orbitals of Lewis bases. The Lewis acid **I** is a strong π base, with the high-lying d donor orbital shown in Figure 1. The importance of this orbital in bonding to unsaturated ligands is evidenced by numerous structural studies.[4a,5,8] These indicate that unsaturated ligands adopt conformations that allow high degrees of overlap of their acceptor orbitals, even in the presence of opposing steric factors.

Accordingly, we sought to prepare analogs of **I** with enhanced σ acidities and diminished π basicities. In principle, any of the three spectator ligands can be modified. However, the nitrosyl group is an outstanding π acceptor, and we know of no other three-electron donor that could further enhance the acidity of the rhenium ion. Cyclopentadienyl ligands can be extensively halogenated, or substituted with electron-withdrawing perfluoroalkyl groups.[9] These would represent viable modification strategies. However, we elected to investigate analogs with fluorinated triarylphosphanes, in part due to our independent interest in highly fluorinated phosphanes for use in fluorous phase catalysis.[10]

In this paper, we describe the synthesis and some surprising reactions of Lewis base adducts of the new chiral rhenium Lewis acids $[(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}]^+$ [**I**-

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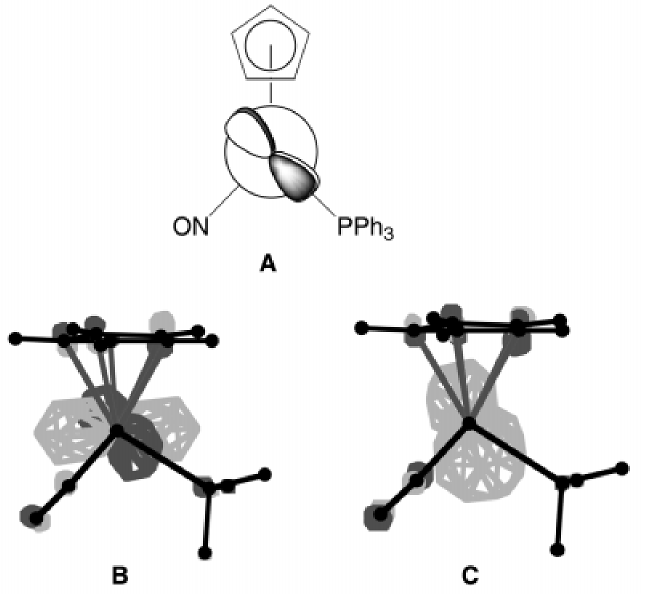


Figure 1. A: idealized d orbital HOMO of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**); B: computed HOMO of the model Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)]^+$ (ref.[25]); C: computed LUMO of the model Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)]^+$ (ref.[25])

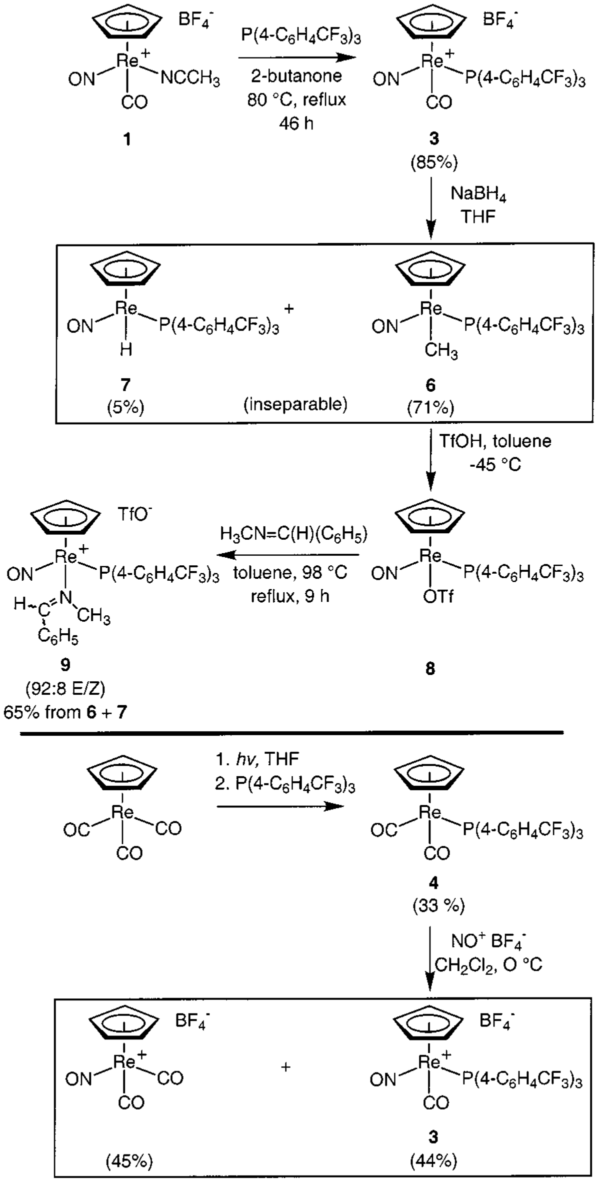
$(CF_3)_3]$ and $[(\eta^5\text{-}C_5H_5)Re(NO)\{P(C_6F_5)_3\}]^+$ (**I**-F_{15}). In the former, the *para* positions of the aryl groups in **I** are substituted with trifluoromethyl groups. A slightly increased σ acidity, and a slightly decreased π basicity, was expected. In the latter, all aryl positions are fluorinated. A greatly enhanced Lewis acidity, and a greatly diminished π basicity, was expected. We also report high-level density functional calculations that allow more quantitative comparisons of the electronic properties of these compounds.

Results

The Nonafluorinated Lewis Acid I-$(CF_3)_3$

The substitution-labile acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(NCCH_3)(CO)]^+BF_4^-$ (**1**) and PPh_3 have previously been shown to react in refluxing ethyl methyl ketone to give the non-fluorinated phosphane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ (**2**).[11] As shown in Scheme 1, compound **1** and the commercially available phosphane $P(4\text{-}C_6H_4CF_3)_3$ were similarly allowed to react. Spectroscopic monitoring showed the need for a somewhat longer reaction time, presumably due to reduced nucleophilicity of the phosphane. After 46 h, workup gave the target complex $[(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(CO)]^+$ BF_4^- (**3**) in 85% yield.

Complex **3** was characterized by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy, as described in the Exp. Sect. As summarized in Table 1, the IR $\tilde{\nu}_{CO}$ and $\tilde{\nu}_{NO}$ values were 30−12 cm^{-1} greater than those of **2**,[11] consistent with decreased π basicity and increased σ acidity. The ^{13}C NMR CO signal was coupled to the phosphorus signal and upfield of that of **2** (Table 1). All aryl carbon atoms showed coupling to the phosphorus atom, and those *ipso* and *ortho* to the trifluoromethyl group were further coupled to the fluorine atoms. Complex **3** could also be prepared by the reaction of dicarbonyl complex $(\eta^5\text{-}C_5H_5)Re(CO)_2\{P(4\text{-}C_6H_4CF_3)_3\}$ (**4**) and $NO^+BF_4^-$ (Scheme 1, bottom). However, due to a competing phosphane displacement to give $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$,[11] the yield was only 44%. Complex **4** could in turn be prepared from $(\eta^5\text{-}C_5H_5)Re(CO)_3$[11] by a standard photolysis/substitution sequence in THF,[12] but our best yield was only 33%.



Scheme 1. Syntheses and reactions of nonafluorinated complexes

The reduction of non-fluorinated **2** by $NaBH_4$ in THF gives the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**5**).[11] As shown in Scheme 1, compound **3** and $NaBH_4$ were analogously treated. Workup gave 97−93:3−7 mixtures of the expected methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(CH_3)$ (**6**) and the unexpected hydride complex $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(H)$ (**7**), as determined by integration of the cyclopentadienyl ^1H

Table 1. Spectroscopic features that reflect the relative electronic properties of the chiral rhenium Lewis acids

Complex	Lewis acid	Lewis base	IR ν_{NO} [cm^{-1}]	IR ν_{CO} [cm^{-1}]	^{13}C{^{1}H} NMR α- or β-C [δ]	J_{CP} [Hz]	^{1}P{^{1}H} NMR [δ]
2	**I**	CO	1760[a]	2001[a]	196.7[b] [c]	8.8	12.4[d]
3	**I**-$(CF_3)_3$	CO	1772[e]	2031[e]	194.4[b]	8.6	14.4[b]
11	**I**-F_{15}	CO	1794[f]	2046[f]	191.2[d]	6.1	−48.0[d]
5	**I**	CH_3	1630[g]	−	−37.5[a]	6.0	25.5[a]
6	**I**-$(CF_3)_3$	CH_3	1663[h]	−	−37.2[b]	7.0	28.9[b]
14	**I**-F_{15}	CH_3	1687[f]	−	−33.1[d]	7.1	−26.5[d]
8	**I**	$C_6H_5(H)C=NCH_3$	1679[e]	−	178.2[b]	2.7	18.4[b]
9	**I**-$(CF_3)_3$	$C_6H_5(H)C=NCH_3$	1703[e]	−	180.0[d]	3.6	22.8[d]

[a] CH_2Cl_2. − [b] CD_3CN. − [c]Redetermined as part of this study for the purpose of obtaining the previously unresolved coupling constant. − [d] [D_6]Acetone. − [e] KBr. − [f] Powder film. − [g] THF. − [h] Hexane.

NMR signals. The combined yield was 76%. Extensive attempts to separate hexane-soluble **6** and **7** by crystallization or TLC were unsuccessful. Hence, they were characterized as a mixture. Similar reductions have been effected with a variety of phosphane ligands,[13,14] but a hydride complex by-product has not been noted earlier. Both **6** and **7** exhibited diagnostic spectroscopic features,[11,15] such as $ReCH_3$ and ReH ^{1}H NMR signals (δ = 0.97 and −9.70) that were coupled to the phosphorus signal (J_{HP} = 6 and 29 Hz). The IR $\tilde{\nu}_{NO}$ value of **6** was greater than that of the non-fluorinated analog **5** (Table 1).[11]

The methyl complex **5** can be converted by various strong acid/solvent combinations into several functional equivalents of the chiral Lewis acid **I**. One of the most convenient is the corresponding triflate,[16] which can be isolated or treated directly with Lewis bases such as imines or thioethers to give adducts of the formula [(η^5-C_5H_5)Re(NO)(PPh_3)(L)]$^+$ TfO$^-$.[17,18] Based upon available data,[19] there would be a reasonable chance that related rhenium hydride complexes would behave similarly. Accordingly, the methyl complex **6** was used as a mixture with **7**.

As shown in Scheme 1, compound **6/7** and TfOH were combined in toluene at −45 °C to generate the new triflate complex (η^5-C_5H_5)Re(NO){P(4-$C_6H_4CF_3$)$_3$}(OTf) (**8**). Complex **8** was not isolated, but directly treated with the imine $H_3CN=C(H)C_6H_5$. Since the analogous reaction of the non-fluorinated triflate is very slow at room temperature,[17] the sample was kept at 98 °C for 9 h. Workup gave the imine complex [(η^5-C_5H_5)Re(NO){P(4-$C_6H_4CF_3$)$_3$}{N(CH_3)=C(H)C_6H_5}]$^+$TfO$^-$ (**9**) as a 92:8 mixture of (*E*)/(*Z*) C=N isomers in 65% yield. Complex **9** was characterized analogously to **3** and **6/7**. The IR $\tilde{\nu}_{NO}$ value was greater than that of the non-fluorinated analog [(η^5-C_5H_5)Re(NO)(PPh_3){N(CH_3)=C(H)C_6H_5}]$^+$TfO$^-$ (**10**; Table 1),[17] which would logically correlate with an enhanced imine carbon electrophilicity. An (*E*) C=N isomer (larger phenyl and bulky rhenium substituents *trans*) also dominated with **10**.[17] These assignments were supported, among other factors, by the relative magnitudes of the $^4J_{HH}$ values of the $H_3CN=CH$ linkages (1.7 vs. 1.2 Hz).[20]

The imine complex **9** was combined with the allylstannane $H_2C=CHCH_2Sn(n\mathrm{Bu})_3$ in CD_2Cl_2 and THF. The former sample was unchanged after 3 d at ambient temperature, as assayed by ^{1}H and ^{31}P NMR. The latter sample was unchanged after 1 d at 60 °C, as assayed by ^{31}P NMR. Carbon−carbon bond-forming reactions of imines and allylstannanes are readily catalyzed by titanium, palladium, and copper Lewis acids.[21] Hence, the modified rhenium Lewis acid **I**-$(CF_3)_3$ remained insufficiently activating, and a more reactive species was sought.

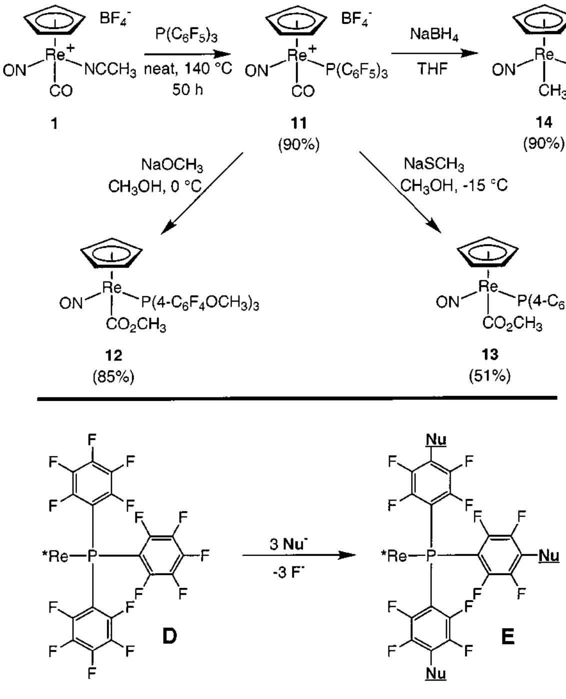
The Pentadecafluorinated Lewis Acid I-F_{15}

A $ClCH_2CH_2Cl$ solution of the acetonitrile complex **1** and the commercially available phosphane $P(C_6F_5)_3$ was kept at 88 °C for 11 h. No reaction occurred, as monitored by IR spectroscopy. A $Cl_2CHCHCl_2$ solution of **1** and $P(C_6F_5)_3$ was similarly kept at 129 °C for 14 h. An IR spectrum indicated that several products had formed. However, the ^{31}P NMR spectrum showed mainly $P(C_6F_5)_3$ (δ = −74.2; 73%), and one new signal that was assigned to the oxide $O=P(C_6F_5)_3$ (δ = −7.9; 27%) based upon the close agreement with the chemical shift in the literature (δ = −7.8).[22]

Reactions were attempted in the absence of solvent. Complex **1** and $P(C_6F_5)_3$ melt at 119 and 107 °C, respectively, and were kept at 140 °C (1.0:1.3 molar ratio) for 10 h. During this time, some of the $P(C_6F_5)_3$ sublimed to the top part of the flask not immersed in the oil bath. Thus, the reaction did not go to completion. Nevertheless, unchanged **1** could be separated from the desired substitution product [(η^5-C_5H_5)Re(NO){$P(C_6F_5)_3$}(CO)]$^+$ BF_4^- (**11**), which was isolated as a yellow powder in 32% yield. Modified reaction vessels were then assayed. The operationally most simple protocol involved starting with 1.5 equivalents of $P(C_6F_5)_3$, inserting some glass wool into the neck of the flask, immersing the flask *completely* in an oil bath (gas release bubbler protruding), and adding a second charge of $P(C_6F_5)_3$ (0.5 equiv.) halfway through the 50 h reaction. This gave **11** in 90% yield on a 3.5-g scale.

Complex **11** was characterized analogously to the other new compounds above. The IR $\tilde{\nu}_{CO}$ and $\tilde{\nu}_{NO}$ values were greater than the P(4-$C_6H_4CF_3$)$_3$ analog **3** (Table 1), indicating a further enhancement of σ acidity and diminution of backbonding into the NO and CO ligands. The ^{13}C NMR CO signal was upfield of that of **3** (Table 1). The ^{31}P NMR signal was downfield of that of $P(C_6F_5)_3$ (δ = −48.0 vs. −74.2 to −75.5).[22] However, only a broad singlet was observed ($w_{1/2}$ = 39−40 Hz), as opposed to the fluorine-coupled pseudoquintuplet (J_{PF} = 35 Hz) of the free phosphane.

The enantiomers of the non-fluorinated carbonyl complex **2** are easily resolved.[11] The first step entails reaction with excess $NaOCH_3$ in methanol to generate the isolable methoxycarbonyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3).[11] Hence, **11** was similarly treated, as shown in Scheme 2. A product precipitated (**12**), but the ^1H NMR spectrum showed both the expected CO_2CH_3 signal (δ = 3.12, s) and an unanticipated resonance (δ = 4.21, t, J_{HF} = 2 Hz). These always appeared in concert, and integrated to a 3:9 ratio. The mass spectrum gave a parent ion consistent with the formula (η^5-C_5H_5)Re(NO){P($C_6F_4OCH_3$)$_3$}(CO_2CH_3), in which a fluorine atom in each aryl ring has been substituted by a methoxy group. The ^{13}C NMR spectrum showed only four aryl signals, requiring a threefold *para* substitution, as well as two types of methoxy signals (δ = 62.9, t, J_{CF} = 4 Hz and 48.9, s). Under optimized conditions, **12** could be obtained in 85% yield.



Scheme 2. Synthesis and reactions of pentadecafluorinated complexes

There is abundant precedent for nucleophilic aromatic substitutions of hexafluorobenzene, and the *para*-fluorine atoms of substituted pentafluorobenzenes.[23,24] However, the conversion of **11** to **12** represents one of the few times that this has been observed with a non-ligating arene in a metal coordination sphere.[24b] In a separate experiment, **11** and $NaOCH_3$ were combined in a 1:1 molar ratio in methanol, and the homogeneous reaction monitored by ^{31}P NMR. Several new signals appeared with chemical shifts close to that of **11** (δ = −50 to −51), and several new signals appeared with chemical shifts close to that of **12** (δ = −33 to −35). These were attributed to intermediate levels of *para* substitution. If methoxide addition to the carbonyl group of **11** were *ir*reversible, this would indicate that fluoride substitution occurs both before and after carbonyl addition.

In order to probe the generality of such threefold substitutions, **11** and the thiolate $NaSCH_3$ were allowed to react in methanol. As shown in Scheme 2, workup gave the sulfur-containing complex (η^5-C_5H_5)Re(NO){P(4-C_6F_4-SCH_3)$_3$}(CO_2CH_3) (**13**) in 51% yield. Interestingly, a methoxy group selectively added to the carbonyl ligand of **11**, whereas thiomethoxy groups selectively displaced fluoride. This structure was supported by a molecular ion peak in the mass spectrum, a correct C/H/N/S microanalysis, and numerous IR and NMR features. For example, the IR $\tilde{\nu}_{CO}$ value of **13** was very similar to that of **12** (1613 vs. 1603 cm^{-1}). Also, the ArS*CH*$_3$ NMR signals of **13** were distinctly upfield of the ArO*CH*$_3$ signals of **12** [^1H: δ = 2.62 (br s) vs. 4.21; $^{13}C\{^1H\}$: δ = 17.0 (t, J_{CF} = 5 Hz) vs. 62.9].

Although the substitution reactions in Scheme 2 are of interest in their own right, they tempered our enthusiasm for the $P(C_6F_5)_3$ ligand as part of a second-generation chiral rhenium Lewis acid. Even if an enantiomer separation not requiring a methoxide addition could be effected, there would be a high probability that similar substitutions would compromise other target reactions or applications in catalysis. Accordingly, it was decided to pursue only one additional reaction in this series, that of **11** and $NaBH_4$. Under conditions comparable to those in Scheme 1, the methyl complex (η^5-C_5H_5)Re(NO){P(C_6F_5)$_3$}(CH_3) (**14**) could be isolated as a crude powder in 90% yield by benzene or toluene extraction of the reaction mixture.

Complex **14** exhibited a number of diagnostic spectroscopic features. These included (1) a ^1H NMR spectrum with methyl (δ = 0.76, d, J_{HP} = 10 Hz) and cyclopentadienyl signals, both very similar to those of **6**, (2) corresponding ^{13}C NMR signals (Table 1), and (3) an intense molecular ion peak in the mass spectrum. However, NMR spectra showed residual benzene or toluene, even after prolonged periods under high vacuum that routinely removed these solvents from other complexes. Treatments with cold pentane improved the purities, but correct microanalyses could never be obtained. Finally, attempts to generate various functional equivalents of the Lewis acid **I**-F_{15} from **14** gave unusual results that would be difficult to interpret without further intensive study.

Computations

There would be obvious approaches to generating highly fluorinated but less substitution-prone triarylphosphanes. Hence, as a justification for possible continued work, we sought computational support for our intuitive estimation of the relative donor/acceptor properties of the fragments **I**, **I**-(CF_3)$_3$, and **I**-F_{15}. One starting point might be to compare model compounds with PH_3 ligands, several of which have been studied previously,[25] to those with PH_xF_{3-x} ligands. Although such systems would contain fewer atoms and electrons and could be investigated at a very high level of rigor, they also constitute less satisfying models for triarylphosphanes.

Accordingly, the geometry of the trimethylphosphane complex (η^5-C_5H_5)Re(NO){P(CH_3)$_3$}(CH_3) was optimized at the level of density functional theory (B3LYP) with the LANL2DZ basis set and an additional set of polarization functions (LANL2DZp) as introduced by Hay and Wadt[26] and implemented in the GAUSSIAN98 program.[27] These results are fully described elsewhere.[26] Next, the phosphorus methyl groups were replaced by C_6H_5, 4-C_6H_4F, and C_6F_5 groups, keeping all geometric features of the (η^5-C_5H_5)Re(NO)(P)(CH_3) entity constant. Note that the second series features *para*-fluorine atoms, as opposed to the larger CF_3 groups of the compounds in Scheme 1.

The PPh_3, P(4-C_6H_4F)$_3$, and P(C_6F_5)$_3$ entities were partially optimized at the HF/LANL2DZ level. The rhenium−phosphorus conformations were allowed to vary, but the HCCC and FCCC torsion angles were fixed at 180.0° − in other words, planar arene rings. This approximation is justified by unpublished results with the hydride complex (η^5-C_5H_5)Re(NO)(PPh_3)(H), for which we have done a full structure optimization and find essentially planar phenyl rings. Next, the methyl groups were replaced by a positive charge, and the orbital energies of the resulting rhenium Lewis acids **I**, **I**-F_3 [roughly equivalent to **I**-(CF_3)$_3$], and **I**-F_{15} calculated**.**

Key data are summarized in Table 2. As would have been intuitively predicted, both the HOMO and LUMO energies decrease with increasing numbers of fluorine atoms. The HOMO energies decrease to a greater extent, indicating that major effect of the fluorine atoms is to diminish π basicity. However, the LUMO energy decrease is still significant, indicating a large enhancement of σ acidity. A mathematical consequence is that the HOMO/LUMO gap steadily *in*creases. Not surprisingly, the energies of other orbitals decrease with increasing fluorine substitution.

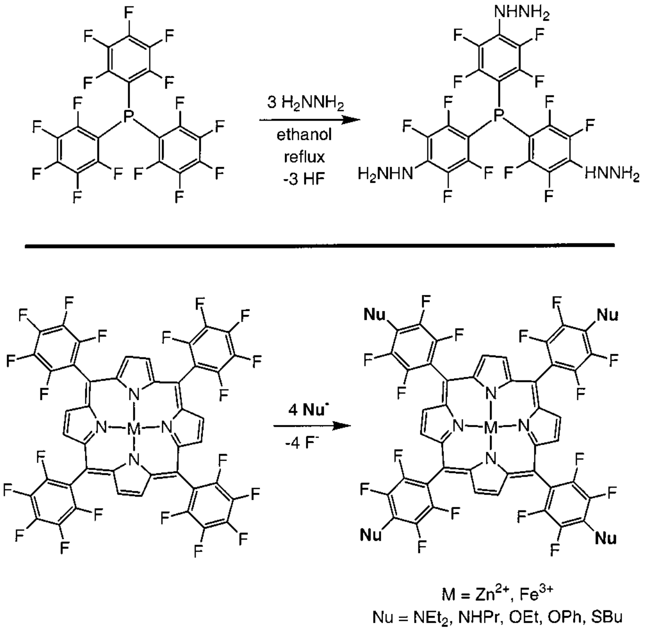
Table 2. Frontier orbital energies [eV] (HF/LANL2DZp) of the chiral Lewis acids

Orbital	Lewis acid **I**	 **I**−(CF_3)$_3$	 **I**−F_{15}
LUMO+1	−1.15	−1.82	−2.19
LUMO	**−3.50**	**−4.09**	**−4.28**
HOMO	**−11.87**	**−12.67**	**−13.42**
HOMO−1	−11.93	−12.86	−13.53
HOMO−2	−12.21	−13.02	−13.80
Δ(LUMO − HOMO)	**8.37**	**8.58**	**9.14**

Discussion

A number of conclusions can be drawn from the above data. With regard to the original objective of this study, the chiral rhenium Lewis acid **I** will clearly require *more* than three highly electronegative aryl substituents in order to activate unsaturated ligands to a broader range of nucleophilic additions. The IR and computational data indicate that **I**-F_{15} should be much more activating than **I**-(CF_3)$_3$, where we had only negative results. However, Scheme 2 shows that this system is prone to nucleophilic displacement of the *para*-fluorine atoms in the aryl rings, a process with much precedent in the organofluorine literature.[23,24] One solution would be to seek substitution-resistant analogs, perhaps with *para*-CF_3 or -C(CF_3)$_3$ groups. The bulk of the latter might help to retard the possible nucleophilic displacement of fluorine atoms at other positions (*ortho*, *meta*).

Despite its markedly attenuated basicity, the perfluorinated phosphane P(C_6F_5)$_3$ has an extensive coordination chemistry.[28] However, to the best of our knowledge, none of these complexes has ever been observed to undergo nucleophilic aromatic substitution. Nonetheless, threefold substitutions do occur with the free ligand.[24a] As shown in Scheme 3, P(C_6F_5)$_3$ and hydrazine cleanly react in refluxing ethanol to give a tris(hydrazino) product. Under analogous conditions, substituted hydrazines gave only partial substitution. Reactions with alkoxides occur at room temperature, but are much more complex. In the case of $NaOCH_3$, the major products are derived from phosphorus−carbon bond cleavage, although the threefold substitution product P(4-$C_6F_4OCH_3$)$_3$ can be isolated in 20% yield.[24a] Thus, the rhenium Lewis acid **I**-F_{15} activates the *para*-fluorine atoms of P(C_6F_5)$_3$ towards substitution.



M = Zn^{2+}, Fe^{3+}
Nu = NEt_2, NHPr, OEt, OPh, SBu

Scheme 3. Some relevant previously reported reactions

Metal-mediated carbon−fluorine bond activation is of particular current interest.[29] We are aware of only one other paper describing nucleophilic aromatic substitutions of σ-pentafluorophenyl groups in metal coordination spheres. The (porphyrin)zinc and -iron compounds illustrated in Scheme 3 (bottom) undergo clean fourfold substitutions with a variety of nucleophiles.[24b] The successful application of sulfur nucleophiles in both this system and ours suggests new ways by which metal complexes might be anchored to thiophilic gold surfaces.

If problems with nucleophilic aromatic substitution can be solved, there are potential advantages associated with perfluorinated triarylphosphanes in chiral transition metal Lewis acids. For instance, many examples of strongly attractive π-stacking interactions between perfluoroarenes and non-fluorinated analogs have recently been documented.[30] This might be a very effective control element for some types of enantioselective reactions. Indeed, Ojima has investigated transformations of various adducts the pentafluorinated iron Lewis acid $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(C_6H_5)_2C_6F_5\}]^+$.[31] This is approximately isostructural to our Lewis acids **I** and **I**-F_{15}, but with just one pentafluorophenyl ring. He often found improved stereoselectivities as compared to the non-fluorinated homolog $[(\eta^5\text{-}C_5H_5)Fe(CO)\{P(C_6H_5)_3\}]^+$. This was attributed to π interactions involving the fluorinated ring.

As noted in the introduction, the Lewis acid **I** might also be modified on the cyclopentadienyl ligand. Indeed, we have reported a number of more electron-rich alkylated derivatives.[32] From a synthesis standpoint, it would be relatively straight-forward to pursue a "tandem activation" strategy. Regardless, this paper concludes our investigations of new types of chiral rhenium Lewis acids that were begun in the USA. Future publications will describe new initiatives that were conceived and fully executed in our new laboratory in Franconia.

Experimental Section

General Data: All reactions were carried out under dry nitrogen using conventional Schlenk techniques. Analytical data were recorded with standard instruments, some of which were described in a previous paper.[17] Rather than enumerate the many small differences between the two locations in which this work was conducted, readers are referred to two dissertations.[33] – Solvents were treated as follows: acetone, distilled from P_2O_5; CH_3CN distilled from P_2O_5; CH_2Cl_2, distilled from Sicapent® (Fluka); ether, distilled from CaH_2; hexane, distilled from K; methanol, distilled from Mg; $[D_6]$acetone, stored over molecular sieves (4 Å). The imine $H_3CN{=}C(H)C_6H_5$ (Aldrich) was vacuum-distilled, $NaSCH_3$ was used as received (Fluka), and $P(4\text{-}C_6H_4CF_3)_3$ and $P(C_6F_5)_3$ were used as received (Strem) or prepared by literature procedures.[33b,34] Other solvents and reagents were used as received from common commercial sources.

$[(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(CO)]^+BF_4^-$ (3). – A: A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(NCCH_3)(CO)]^+BF_4^-$ (**1**;[11] 0.194 g, 0.429 mmol) and fitted with a condenser that was joined to an N_2 line/oil bubbler. Ethyl methyl ketone (20 mL) was added. The solution was refluxed (oil bath) with stirring for 46 h, and allowed to cool. Hexane (ca. 200 mL) was added. The yellow solid was collected by filtration, washed with pentane (20 mL), and dried by oil pump vacuum to give **3** (0.313 g, 0.363 mmol, 85%). – **B:** A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(CO)_2\{P(4\text{-}C_6H_4CF_3)_3\}$ (preparation below; 1.121 g, 1.449 mmol) and CH_2Cl_2 (50 mL), and cooled to 0 °C. Solid $NO^+BF_4^-$ (0.204 g, 1.74 mmol; freshly washed with 20 mL of CH_2Cl_2) was added with stirring. The ice bath was allowed to warm. After 30 h, solvent was removed by rotary evaporation. THF (250 mL) was added. The bright yellow powder was collected on a frit to give $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+\ BF_4^-$ (0.274 g, 0.647 mmol, 45%).[11] The filtrate was concentrated (ca. 2 mL), and hexane (50 mL) was added. The yellow solid was collected on a frit, washed with CH_2Cl_2/hexane (20 mL, 20:80 v/v) and pentane (20 mL), and dried by oil pump vacuum to give **3** (0.545 g, 0.632 mmol, 44%), m.p. 236–237 °C (dec.). – $C_{27}H_{17}BF_{13}NO_2PRe$ (862.4): calcd. C 37.60, H 1.99; found C 37.04, H 2.01. – IR (cm^{-1}, CH_2Cl_2/KBr): $\tilde{\nu}_{CO}$: 2027/2031 (s); $\tilde{\nu}_{NO}$: 1772/1772 (s). – NMR (δ, CD_3CN):[35] ^1H: 7.95–7.86 (m, 6 H of 3 C_6H_4), 7.63–7.52 (m, 6 H of 3 C_6H_4), 5.96 (s, C_5H_5); $^{13}C\{^1H\}$: 194.4 (d, $^2J_{CP} = 8.6$, CO), 135.2 (d, $^2J_{CP} = 12.3$, *o*-C_6H_4), 135.1 (d, $^1J_{CP} = 58.9$, *i*-C_6H_4), 134.6 (qd, $^2J_{CF} = 33$, $^4J_{CP} = 3$, *p*-C_6H_4), 127.6 (qd, $^3J_{CF} = 3.9$, $^3J_{CP} = 11.9$, *m*-C_6H_4), 124.5 (q, $^1J_{CF} = 272$, CF_3), 96.1 (s, C_5H_5); $^{31}P\{^1H\}$: 14.4 (s).

Reduction of 3: A Schlenk flask was charged with **3** (0.114 g, 0.132 mmol), THF (20 mL), and $NaBH_4$ (0.015 g, 0.40 mmol). The mixture was stirred for 2 h, and solvent was removed by oil pump vacuum. Benzene (100 mL) was added, and the sample was filtered through silica gel. Solvent was removed by rotary evaporation. The residue was dissolved in hexane (50 mL), and the solution was slowly concentrated by rotary evaporation. An orange powder formed, which was collected on a frit and dried under oil pump vacuum to give a 93:7 mixture (0.078 g) of $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(CH_3)$ (**6**) (0.073 g, 0.093 mmol, 71%) and $(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}(H)$ (**7**) (0.005 g, 0.007 mmol, 5%), m.p. 165–166 °C. – IR (cm^{-1}, THF/hexane): $\tilde{\nu}_{NO}$: 1645/1663 (s). – MS:[36] 763 [**6**$^+$] (100%), 749 [**7**$^+$] (6%), 748 [**6**$^+$ – CH_3] (23%). – NMR (**6**; δ, $CDCl_3$):[35] ^1H: 7.77–7.67 (m, 6 H of 3 C_6H_4), 7.59–7.48 (m, 6 H of 3 C_6H_4), 5.00 (s, C_5H_5), 0.97 (d, $^3J_{CP} = 6.1$, CH_3); $^{13}C\{^1H\}$: 139.9 (d, $^1J_{CP} = 48.6$, *i*-C_6H_4), 133.8 (d, $^2J_{CP} = 11.1$, *o*-C_6H_4), 132.4 (qd, $^2J_{CF} = 33$, $^4J_{CP} = 2$, *p*-C_6H_4), 125.5 (qd, $^3J_{CF} = 3.7$, $^3J_{CP} = 10.1$, *m*-C_6H_4), 123.5 (q, $^1J_{CF} = 273$, CF_3), 90.0 (s, C_5H_5), –37.2 (d, $^2J_{CP} = 7.0$, CH_3); $^{31}P\{^1H\}$: 28.9 (s). – NMR (**7**, partial; δ, $CDCl_3$): ^1H: 5.02 (s, C_5H_5), –9.70 (d, $^2J_{CP} = 29.3$, ReH); $^{13}C\{^1H\}$: 85.8 (s, C_5H_5); $^{31}P\{^1H\}$: 31.6 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)\{P(4\text{-}C_6H_4CF_3)_3\}\{N(CH_3){=}C(H)C_6H_5\}]^+TfO^-$ (9): A Schlenk flask was charged with a **6/7** mixture (0.070 g, 0.092 mmol) and toluene (10 mL), and cooled to –45 °C (CH_3CN/CO_2). Then TfOH (0.008 mL, 0.09 mmol) was added dropwise with stirring. After 10 min, $H_3CN{=}C(H)C_6H_5$ (0.056 mL, 0.46 mmol) was added. The flask was placed in a 98 °C bath, and a precipitate began to form. After 9 h, the mixture was cooled to room temperature and hexane (50 mL) was added. The yellow-orange powder was collected by filtration, washed with hexane (10 mL), and dried by oil pump vacuum to give **9** as a 92:8 (*E*)/(*Z*) mixture (0.060 g, 0.059 mmol, 65%), m.p. 238–239 °C (dec.).[37] – $C_{35}H_{26}BF_{12}N_2O_4PReS$ (1026.6): calcd. C 41.38, H 2.58; found C 40.76, H 2.66. – IR (cm^{-1}, CH_2Cl_2/KBr): $\tilde{\nu}_{NO}$: 1701/1703 (s). – MS:[36] 866.8 (100) $[(C_5H_5)Re(NO)\{P(C_6H_4CF_3)_3\}\{N(CH_3) = C(H)C_6H_5\}]^+$, 747.9 (62) $[(C_5H_5)Re(NO)\{P(C_6H_4CF_3)_3\}]^+$. – NMR (δ, $[D_6]$acetone):[35] ^1H: 8.45/8.69 (d/br s, $^4J_{HH} = 1.7$, *E*/*Z* =CH), 8.05–7.92 (m, 5 H of 3 C_6H_4 + C_6H_5), 7.85–7.71 (m, 6 H of 3 C_6H_4 + C_6H_5), 7.61–7.40 (m, 4 H of 3 C_6H_4 + C_6H_5), 7.19–7.12 (2 H of C_6H_5), 6.03/6.09 (2 s, *E*/*Z* C_5H_5), 4.01/3.65 (2 d, $^4J_{HH} = 1.7/1.2$, *E*/*Z* NCH_3);[20] $^{13}C\{^1H\}$: 180.0 (d, $^3J_{CP} = 3.6$, C=N), 136.1 (d, $^1J_{CP} = 53.0$, *i*-C_6H_4), 135.5 (d, $^2J_{CP} = 11.9$, *o*-C_6H_4), 133.7 (dq, $^4J_{CP} = 2.4$, $^2J_{CF} = 32.8$, *p*-C_6H_4), 127.4 (dq, $^3J_{CP} = 11.1$, $^3J_{CF} = 3.8$, *m*-C_6H_4), 132.8, 130.5, 129.4, 129.0 (4s, *C_6H_5*), 94.2/94.7 (2 s, *E*/*Z* C_5H_5), 56.1 (s, CH_3). $^{31}P\{^1H\}$: 22.8/20.8 (2 s, *E*/*Z*).

$[(\eta^5\text{-}C_5H_5)Re(NO)\{P(C_6F_5)_3\}(CO)]^+BF_4^-$ (11): A 5-mL flask was charged with **1** (1.800 g, 4.12 mmol), $P(C_6F_5)_3$ (3.397 g, 6.39 mmol), and a stir bar. The neck was fitted with a glass wool plug and a nitrogen bubbler. The flask was placed beneath the surface of a 140 °C oil bath (bubbler protruding). After 27 h, additional $\mathrm{P(C_6F_5)_3}$ (1.103 g, 2.07 mmol) was added. After another 23 h, the bath was removed. The solid that formed upon cooling was extracted with $\mathrm{CH_3CN}$ (70 mL). The extract was filtered through Celite and concentrated to 5 mL by rotary evaporation. A hexane/ether mixture (70 mL, 1:1 v/v) was added. The yellow precipitate was collected on a glass frit (G3) and washed with hexane (40 mL) and $\mathrm{CH_2Cl_2}$/hexane (ca. 200 mL, 4:5 v/v) until the filtrate was colorless. The yellow powder was dried by oil pump vacuum to give **11** (3.453 g, 3.72 mmol, 90%), m.p. 246−248 °C. − $\mathrm{C_{25}H_5BF_{18}NO_2PRe}$ (921.3): calcd. C 31.05, H 0.54, N 1.51; found C 31.41, H 0.54, N 1.89. − IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2/CH_3CN}$/powder film): $\tilde{\nu}_{\mathrm{CO}}$: 2043/2047/2046 (s); $\tilde{\nu}_{\mathrm{NO}}$: 1794/1794/1794 (s). − MS:[36] 842 (100) $[\mathrm{(C_5H_5)Re(NO)\{P(C_6F_5)_3\}(CO)}]^+$, 814 (15) $[\mathrm{(C_5H_5)Re(NO)\{P(C_6F_5)_3\}}]^+$, 310 (15) $[\mathrm{(C_5H_5)Re(NO)(CO)}]^+$. − NMR (δ):[35] ^{1}H ($[\mathrm{D_6}]$acetone/$\mathrm{CD_3CN}$): 6.33/5.94[38] (s, $\mathrm{C_5H_5}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($[\mathrm{D_6}]$acetone/$\mathrm{CD_3CN}$): 191.2/191.3 (d, $^2J_{\mathrm{CP}}$ = 6.1/6.8, CO), 148.1/148.3 (dm, $^1J_{\mathrm{CF}}$ = 249.1/247, *m*-$\mathrm{C_6F_5}$), 146.1/146.5 (dm, $^1J_{\mathrm{CF}}$ = 260.0/261, *p*-$\mathrm{C_6F_5}$), 139.3/139.6 (dm, $^1J_{\mathrm{CF}}$ = 258.6/252, *o*-$\mathrm{C_6F_5}$), 104/− (dm, $^1J_{\mathrm{CP}}$ = 58.5/−, *i*-$\mathrm{C_6F_5}$),[39] 97.2/97.1 (s, $\mathrm{C_5H_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ ($[\mathrm{D_6}]$acetone/$\mathrm{CD_3CN}$): −48.0/−48.5 (br s, $w_{1/2}$ = 40/39 Hz); $^{19}\mathrm{F}\{^1\mathrm{H}\}$ ($[\mathrm{D_6}]$acetone):[39] −129.0 (m, *o*-$\mathrm{C_6F_5}$), −144.3 (tt, $^3J_{\mathrm{FF}}$ = 20, $^4J_{\mathrm{FF}}$ = 8, *p*-$\mathrm{C_6F_5}$), −152.2 (s, $\mathrm{BF_4}$), −158.8 (t, $^3J_{\mathrm{FF}}$ = 20, *m*-$\mathrm{C_6F_5}$).

$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)\{P(4\text{-}C_6F_4OCH_3)_3\}(CO_2CH_3)}$ (12): A Schlenk flask was charged with **11** (0.8830 g, 0.951 mmol) and methanol (10 mL) and cooled to 0 °C. Then $\mathrm{NaOCH_3}$ (5.4 M in methanol; 1.232 mL. 6.65 mmol) was added. The sample was stirred for 2 h at 0 °C. The yellow precipitate was collected on a glass frit (G3), washed with methanol (15 mL) and water (20 mL), and dried by oil pump vacuum to give **12** (0.7345 g, 0.808 mmol, 85%), m.p. 131−134 °C (dec.). − $\mathrm{C_{28}H_{17}F_{12}NO_6PRe}$ (908.6): calcd. C 37.01, H 1.89; N 1.54; found C 36.73, H 1.93; N 1.35. − IR ($\mathrm{cm^{-1}}$, powder film): $\tilde{\nu}_{\mathrm{CO}}$: 1613 (s); $\tilde{\nu}_{\mathrm{NO}}$: 1695 (s). − MS:[36] 909 (5) [**12**$^+$], 878 (100) [**12**$^+$ − $\mathrm{OCH_3}$], 850 (8) [**12**$^+$ − $\mathrm{CO_2CH_3}$], 568 (3) $[\mathrm{P(C_6F_4OCH_3)_3}]^+$. − NMR (δ, $[\mathrm{D_6}]$acetone):[35] ^{1}H: 5.44 (s, $\mathrm{C_5H_5}$), 4.21 (t, $^5J_{\mathrm{HF}}$ = 2, 3 $\mathrm{C_6F_4OCH_3}$), 3.12 (s, $\mathrm{CO_2CH_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: 189.1 (d, $^2J_{\mathrm{CP}}$ = 12.9, $C\mathrm{O_2CH_3}$), 148.4 (dm, $^1J_{\mathrm{CF}}$ = 248.7, *m*-$\mathrm{C_6F_4}$), 141.3 (dm, $^1J_{\mathrm{CF}}$ = 228.6, *o*-$\mathrm{C_6F_4}$), 142.2 (t, *p*-$\mathrm{C_6F_4}$),[40] 106.0 (m, *i*-$\mathrm{C_6F_4}$), 94.9 (s, $\mathrm{C_5H_5}$), 62.9 (t, $^4J_{\mathrm{CF}}$ = 4.1, $\mathrm{C_6F_4O}C\mathrm{H_3}$), 48.9 (s, $\mathrm{CO_2}C\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$: −36.4 (br s, $w_{1/2}$ = 23 Hz).

$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)\{P(4\text{-}C_6F_4SCH_3)_3\}(CO_2CH_3)}$ (13): A Schlenk flask was charged with **11** (0.2000 g, 0.215 mmol) and methanol (8 mL). The sample was stirred to dissolve all **11**, and then cooled to −15 °C (ice/NaCl bath). Then $\mathrm{NaSCH_3}$ (0.1056 g, 1.507 mmol) was added with stirring. After 10 min, the yellow precipitate was collected on a glass frit (G3) and dried by oil pump vacuum to give **13** (0.1040 g, 0.108 mmol, 51%), m.p. 140−141 °C (dec.). − $\mathrm{C_{28}H_{17}F_{12}NO_3PReS_3}$ (956.8): calcd. 35.15, H 1.79; N 1.46, S 10.05; found C 35.44, H 1.71, N 1.16, S 10.32. − IR ($\mathrm{cm^{-1}}$, powder film): $\tilde{\nu}_{\mathrm{CO}}$: 1603 (s); $\tilde{\nu}_{\mathrm{NO}}$: 1718 (s). − MS:[36] 958 (2) [**13**$^+$ + H], 926 (100) [**13**$^+$ − $\mathrm{OCH_3}$], 898 (20) [**12**$^+$ − $\mathrm{CO_2CH_3}$], 616 (10) $[\mathrm{P(C_6F_4SCH_3)_3}]^+$. − NMR (δ, $\mathrm{CDCl_3}$):[35] ^{1}H: 5.40 (s, $\mathrm{C_5H_5}$), 3.25 (s, $\mathrm{OCH_3}$), 2.62 (br. s, $w_{1/2}$ = 4 Hz, 3 $\mathrm{SCH_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: 190.1 (d, $^2J_{\mathrm{CP}}$ = 13, $C\mathrm{O_2CH_3}$), 146.3 (dm, $^1J_{\mathrm{CF}}$ = 254.2, *m*-$\mathrm{C_6F_4}$), 146.1 (dm, $^1J_{\mathrm{CF}}$ = 253.4, *o*-$\mathrm{C_6F_4}$), 121.6 (t, $^2J_{\mathrm{CF}}$ = 18.1, *p*-$\mathrm{C_6F_4}$), 111.0 (m, *i*-$\mathrm{C_6F_4}$), 94.0 (s, $\mathrm{C_5H_5}$), 49.5 (s, $\mathrm{OCH_3}$), 17.0 (t, $^4J_{\mathrm{CF}}$ = 4.8, $\mathrm{SCH_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$: −34.1 (br s, $w_{1/2}$ = 26 Hz).

$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(NO)\{P(C_6F_5)_3\}(CH_3)}$ (14): A Schlenk flask was charged with **11** (0.300 g, 0.323 mmol) and THF (15 mL) and (as an extra precaution) freeze-pump-thaw degassed (3 ×). Then $\mathrm{NaBH_4}$ (0.026 g, 0.69 mmol) was added with stirring. After 10 min, the THF was removed by oil pump vacuum. Benzene (10 mL) was added, and the sample was filtered through a short silica gel plug on a glass frit (G3). Solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **14** as an orange powder (0.241 g, 0.291 mmol, 90%) that still contained benzene (see text). The sample was suspended in cold pentane (10 mL), and analogously collected by filtration and dried. This gave **14** with less but still detectable residual solvent (0.225 g, 0.175 mmol, 84%), m.p. 141−143 °C (dec.). − $\mathrm{C_{24}H_8F_{15}NOPRe}$ (828.5): calcd. C 34.79, H 0.97, N 1.69; found C 35.79, H 1.32, N 1.75. − IR ($\mathrm{cm^{-1}}$, powder film): $\tilde{\nu}_{\mathrm{NO}}$: 1687 (s). − MS:[36] 829 (100) [**14**$^+$], 297 (90) $[\mathrm{(C_5H_5)Re(NO)(CH_3)}]^+$. − NMR (δ, $[\mathrm{D_6}]$acetone):[35] ^{1}H: 5.28 (s, $\mathrm{C_5H_5}$), 0.76 (d, $^3J_{\mathrm{HP}}$ = 9.5, $\mathrm{CH_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: 147.9 (dm, $^1J_{\mathrm{CF}}$ = 254.8, *m*-$\mathrm{C_6F_5}$), 144.2 (dm, $^1J_{\mathrm{CF}}$ = 250.3, *p*-$\mathrm{C_6F_5}$), 138.6 (dm, $^1J_{\mathrm{CF}}$ = 254.7, *o*-$\mathrm{C_6F_5}$), 109.7 (m, *i*-$\mathrm{C_6F_5}$),[39] 93.3 (s, $\mathrm{C_5H_5}$), −33.1 (d, J_{CP} = 7.1, $\mathrm{CH_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$: −26.5 (br s, $w_{1/2}$ = 16 Hz).

$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(CO)_2\{P(4\text{-}C_6H_4CF_3)_3\}}$ (4): A quartz tube was charged with $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(CO)_3}$ (0.584 g, 1.74 mmol)[11] and THF (250 mL), and placed in an ice/water bath. The solution was irradiated with a 450-W Hanovia high-pressure mercury-vapor lamp. The sample was continuously stirred and purged with $\mathrm{N_2}$. The formation of $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Re(CO)_2(THF)}$[12a] was verified by IR ($\tilde{\nu}_{\mathrm{CO}}$: 1908, 1836 $\mathrm{cm^{-1}}$). After 3 h, the lamp was turned off and $\mathrm{P(4\text{-}C_6H_4CF_3)_3}$ (1.01 g, 2.17 mmol) was added to the brown solution. After 72 h, solvent was removed by oil pump vacuum. Hexane (ca. 200 mL) was added, and the mixture was filtered through Celite. The filtrate was slowly concentrated by rotary evaporation. Off-white crystals formed, which were collected by filtration, washed with pentane, and dried by oil pump vacuum to give **4** (0.442 g, 0.580 mmol, 33%), m.p. 187−188 °C (dec.). − $\mathrm{C_{28}H_{17}F_9O_2PRe}$ (773.6): calcd. C 43.47, H 2.21; found C 43.27, H 2.26. − IR ($\mathrm{cm^{-1}}$, THF/$\mathrm{CH_2Cl_2}$): $\tilde{\nu}_{\mathrm{CO}}$: 1938/1937 (s), 1874/1869 (s). − NMR (δ, $\mathrm{CDCl_3}$):[35] ^{1}H: 7.72−7.65 (m, 6 H of 3 $\mathrm{C_6H_4}$), 7.58−7.47 (m, 6 H of 3 $\mathrm{C_6H_4}$), 5.00 (s, $\mathrm{C_5H_5}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: 200.8 (d, $^2J_{\mathrm{CP}}$ = 8.5, 2CO), 141.3 (d, $^1J_{\mathrm{CP}}$ = 50.0, *i*-$\mathrm{C_6H_4}$), 132.2 (d, $^2J_{\mathrm{CP}}$ = 10.0, *o*-$\mathrm{C_6H_4}$), 132.2 (qd, $^2J_{\mathrm{CF}}$ = 33, $^4J_{\mathrm{CP}}$ = 2, *p*-$\mathrm{C_6H_4}$), 125.3 (qd, $^3J_{\mathrm{CF}}$ = 3.7, $^3J_{\mathrm{CP}}$ = 10.5, *m*-$\mathrm{C_6H_4}$), 123.5 (q, $^1J_{\mathrm{CF}}$ = 273, $\mathrm{CF_3}$), 83.8 (s, $\mathrm{C_5H_5}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$: 33.9 (s).

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[36] (+)-FAB, 3-NBA/CH$_2$Cl$_2$ or 3-NBA matrix, *m/z* (%) for most intense peak of isotope envelope.

[37] Some preparations gave small amounts of a by-product believed to be the methylamine complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re(NO)}\{\text{P(4-C}_6\text{H}_4\text{CF}_3)_3\}\{\text{N(CH}_3)\text{H}_2\}]^+\text{TfO}^-$, presumably derived from inadvertent hydrolysis of the C=N linkage at some stage (PPh$_3$ analog: M. A. Dewey, D. A. Knight, D. P. Klein, A. M. Arif, J. A. Gladysz, *Inorg. Chem.* **1991**, *30*, 4995−5002). This more-

soluble species could be separated from **9** by crystallization from acetone/hexanes. − MS:[36] 778.7 (100) $[(C_5H_5)Re(NO)\{P(C_6H_4CF_3)_3\}\{N(CH_3)H_2\}]^+$, 747.8 (65) $[(C_5H_5)Re(NO)\{P(C_6H_4CF_3)_3\}]^+$. − NMR (δ, CD_3COCD_3, partial): ^1H: 5.79 (s, C_5H_5); $^{13}C\{^1H\}$: 93.3 (s, C_5H_5); $^{31}P\{^1H\}$: 22.3.

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